

Thermal desorption of CH₄ retained in CO₂ ice

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Abstract CO₂ ices are known to exist in different astrophysical environments. In spite of this, its physical properties (structure, density, refractive index) have not been as widely studied as those of water ice. It would be of great value to study the adsorption properties of this ice in conditions related to astrophysical environments. In this paper, we explore the possibility that CO₂ traps relevant molecules in astrophysical environments at temperatures higher than expected from their characteristic sublimation point. To fulfil this aim we have carried out desorption experiments under High Vacuum conditions based on a Quartz Crystal Microbalance and additionally monitored with a Quadrupole Mass Spectrometer. From our results, the presence of CH₄ in the solid phase above the sublimation temperature in some astrophysical scenarios could be explained by the presence of several retaining mechanisms related to the structure of CO₂ ice.

Keywords methods: laboratory — techniques: miscellaneous — planets and satellites: general — ISM: general

1 Introduction

The physical properties of ices present in astrophysical scenarios are related to their porous structure. One of

them is the ice capacity to retain molecules above their characteristic sublimation temperature.

This feature is relevant in the physics of gases present in atmospheres of some astrophysical environments, for instance: Massive stars (Viti et al. 2004), giant planets (Hersant et al. 2004) and objects of the Solar System such as Triton (Rubincam 2003).

It is known that water ice is the most abundant molecule in interstellar icy grain mantles and on some objects of our solar system, but CO₂ has been revealed as another abundant molecule (de Graauw et al. 1996; Gürtler et al. 1996), and is even the major component in some astrophysical scenarios, such as, for instance, Mars in our Solar System. CO₂ has been studied from several points of view: Its optical constants (n , k); integrated absorption coefficient (A); spectral properties before and after UV photolysis and ion irradiation, using infrared spectroscopy, and density have been widely derived in previous works (Wood & Roux 1982; Hudgins et al. 1993; Ehrenfreund et al. 1997; Baratta et al. 1998).

In spite of the results referred to above, it is necessary to continue researching to improve our knowledge of the relationship between the structure and the adsorption properties of CO₂ at low temperatures. This is important because it can influence the abundance of volatile molecules such as CH₄, N₂, CO, etc.

One of the first experiments performed in this area is that of Schulze & Abe (1980). They studied the density as a function of the deposition temperature, relating this parameter with the adsorption capacity of CO₂ ice, from 4 to 87 K. They found that the density increases from $\sim 1.0 \text{ g cm}^{-3}$ to 1.7 g cm^{-3} as the deposition temperature increases. As a result, the adsorption capacity decreases with the increasing deposition temperature. They refer to density as the structure including voids (true density). In this paper, we will use the same definition.

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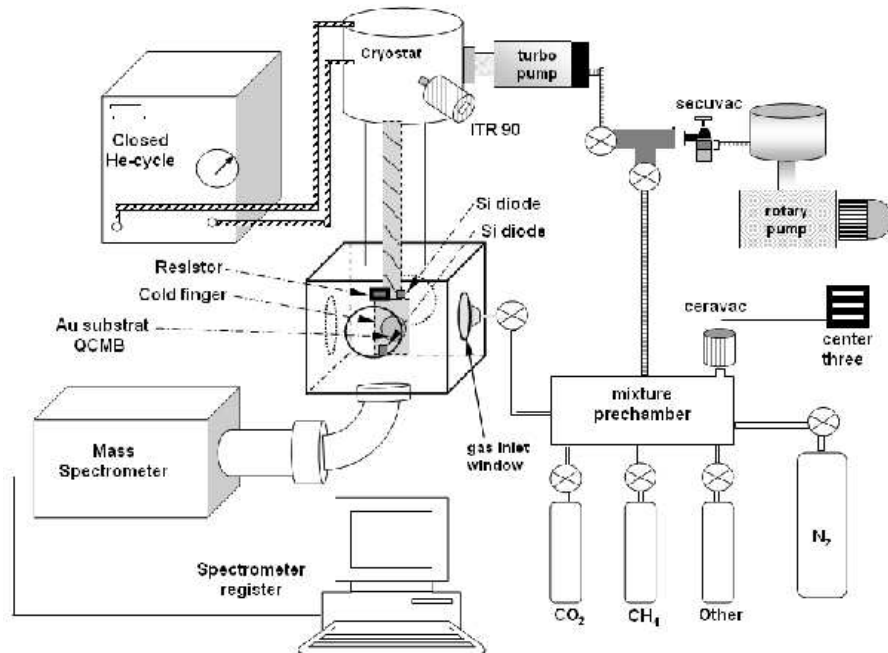


Fig. 1.— Experimental setup.

To the best of our knowledge, there have been no additional experiments designed to determine the relationship between the structure and the adsorption capacity of CO_2 ice. With the aim of filling this gap, our laboratory is currently carrying out an exhaustive set of experiments in order to understand the properties of the CO_2 structure in different conditions.

The experiments presented in this paper are intended to better understand the behaviour of relevant astrophysical molecules co-deposited with CO_2 and subsequently heated at a fixed rate. A similar technique, Thermal Programmed Desorption (TPD) performed under Ultra High Vacuum (UHV) conditions, has been used to study water ice structure (Collings et al. 2003, 2004). Among the structural studies on water it is necessary to highlight those where the porosity of its amorphous form has been studied with other techniques (Bar-Nun et al. 1985; Jenniskens & Blake 1996; Dohnalek et al. 2003). The results and the models used for water by those authors, have been taken as a starting point despite the fact that the differences between both molecules are known.

Concerning to water ice, a first result observed is that when the temperature of deposition increases, the amount of trapped gas decreases. This is a general trend also found by Schulze & Abe (1980) for CO_2 . It is also found that a first release of molecules is shifted to higher temperatures than their characteristic sublimation temperature; a second release of molecules is

also recorded at temperatures related with a structural change (phase change) in water ice ($\sim 135 - 150$ K); and a last release at the water sublimation temperature ($\sim 160 - 175$ K).

All these features are related to the structure of water which is known to change with temperature. The experiments of Stevenson et al. (1999) and Jenniskens & Blake (1996) show a continuous variation of the amorphous structure from 10 K up to the crystallization temperature to cubic form at around 140 K.

This variation of structure can be seen in the model presented by Collings et al. (2003) based on TPD experiments and RAIR spectra. The desorption process during crystallization was previously studied by Smith et al. (1997) proposing a mechanism known as “molecular volcano”.

Once the main results have been shown, it is important to highlight that these experiments are of great importance in many aspects of astrophysics. An interesting example is that of Fraser & van Dishoeck (2004), who showed the relationship between the mechanisms of chemical and physical adsorption with surface chemistry under interstellar and protostellar conditions. It could be also used to model the sublimation of ices as done by Viti et al. (2004) for ices present in solid water near massive protostars.

The models used by Viti et al. (2004) combine codeposition and layered deposition experiments performed

by Collings et al. (2004). In spite of both kinds of experiments have been used it seems from comparing the observational data with laboratory experiments that the water ice shows a compact structure that is best represented by a layered model rather than a mixed ice (Keane et al. 2001; Pontoppidan et al. 2003; Fraser et al. 2004; Guillot & Guissani 2004; Palumbo 2006). Along the same lines, this leads to the suggestion that species such as CO, CO₂, OCS, CH₃OH are partially segregated. However, as Raut et al. (2007) have shown, this question could be not completely clear. Then, the possibility exists that at first the ices were mixed. With this in mind, our objective is to improve the means at our disposal with which to improve our knowledge of the chemical and physical interactions of the observed molecules in space.

Since the existence in different astrophysical environments of CO₂ ices is known, it is relevant to study how their adsorption characteristics can influence the composition of several environments depending on their physical conditions.

In this paper, the desorption behaviour of CH₄ from CO₂ during thermal processing is presented. The experimental setup and the experimental procedure are explained in Section 2. In Section 3 the main results are shown and discussed. Finally, the conclusions reached on the influence of temperature on CO₂ structure are presented in Section 4.

2 Laboratory experiments

2.1 Experimental SETUP

The basic components of our experimental configuration (Figure 1) to carry out these experiments are a high vacuum and low temperature system, a quartz crystal microbalance (QCM), a laser and a quadrupole mass spectrometer (QMS). The main component is a high vacuum chamber ($P \leq 10^{-7}$ mbar) whose pressure conditions are obtained with a rotatory pump ($\sim 10^{-3}$ mbar) backing a Leybold TurboVac 50 pump.

The first stage of a closed-cycle He cryostat (40 K) thermally connected to a shield protector acts as a cryopump providing a pressure in the chamber below 10^{-7} mbar measured with an ITR IoniVac transmitter (5 % in accuracy). The second stage of the cryostat is named *cold finger* and is able to achieve 10 K. Below this, is located the substrate bearing a QCM (gold plated surface) in thermal contact with the cold finger.

The temperature in the sample (QCM) is operated by the Intelligent Temperature Controller ITC 503S (Oxford Instruments), using the feedback of a silicon

diode sensor (Scientific Instruments) located just behind it, that lets the temperature vary between 10 to 300 K with an accuracy of 1 K. Another sensor is located at the end of the cryostat second stage, on the edge of the sample holder in order to monitor the behaviour of the system.

Gases or mixtures under study are prepared in a pre-chamber in a proportion estimated from their partial pressures measured with a Ceravac CTR 90 (Leybold Vacuum) whose accuracy is 0.2 %, provided with a ceramic sensor not influenced by the gas type. The gases enter the chamber through a needle valve (Leybold D50968) that regulates the gas flow while the QMS (AccuQuad RGA 100 with a resolution of ~ 0.5 amu) allows us to verify the proportion of gases in the sample (by dividing, in the mass spectra, the area of methane by the area of carbon dioxide).

2.2 Experimental procedure

Thermal desorption experiments were carried out to analyze sublimation temperature of pure and mixed frozen gases. The following chemicals have been used in this research: CH₄ – 99.9995, CO₂ – 99.998 (Praxair), N₂ – 99.999 (Carbueros Metálicos). Pure gases and mixtures of gases are prepared for deposition in the pre-chamber. In all the cases the overall pressure was fixed at 90 mbar.

In order to obtain the desired temperature and to reduce contamination, the procedure to cool down the cold finger is as follows: The cryostat is connected and at the same time the resistor on the cold finger is turned on at a certain voltage to maintain a temperature in the cold finger (200 K) over the deposition temperature of undesired gases (mainly H₂O and CO₂). After one hour, when the pressure is around 5×10^{-8} mbar, the current through the resistor is turned off. This procedure allows us to ensure that only a negligible amount of contaminants remain in the chamber, taking into account that a typical experiment lasts 2 hours at maximum. The deposition temperature (15 K) is achieved in a few minutes (to again reduce contamination).

Once the temperature is fixed, the needle valve is opened during 1 minute, to fill the chamber with the selected pure gas or mixture of gases keeping the pumps on. Molecules replenish the chamber randomly and are deposited onto the QCM (background deposition). The amount of deposit is enough to assume that the continuum is negligible and does not saturate the mass spectrometer (10^{-4} mbar). In all cases the rate of ice deposition is around 1 micrometer per hour, measured using a laser (He-Ne) interferometry and the QCM frequency variations.

Once deposited, our experiments were performed by heating the substrate at a constant rate of 1 K min^{-1} , the vacuum system working continuously, monitoring the molecules present in the chamber during desorption with the QMS and checking the molecules released with the QCMB. The refractive indexes used for calculations were obtained in our laboratory in a series of experiments (Satorre et al. in preparation).

3 Results and discussion

In order to study the capacity of CO_2 to trap CH_4 in its structure we have performed experiments on thermal desorption for pure CH_4 and CO_2 gases and for mixtures of both them. In the first group of experiments, both molecules were deposited as a pure film onto the substrate and in the second set, both gases were co-deposited in a proportion of 95:5 ($\text{CO}_2:\text{CH}_4$). These three experiments are represented in Figure 2, where frequency of the QCMB is plotted versus temperature.

For the thermal process of pure CO_2 (Figure 2, left panel) we can observe an initial interval (35 to 80 K) where the frequency varies linearly with the temperature as expected for our QCMB (in this specific interval of temperatures) when no release of material takes place. In a second interval, from 80 to 90 K, a sharp increase of frequency is due to the CO_2 desorption from the QCMB. Finally, at 91 K CO_2 stops its desorption and the increase in frequency is again caused by a linear temperature effect. Hereafter we will take as the desorption temperature the point in the plot where the slope, after increasing, changes abruptly. In the case of CH_4 (Figure 2, center panel), it is shown that the desorption occurs at 38 K, and further on, the variation is again due to temperature effect. In both cases, pure CO_2 and CH_4 , only one interval of desorption from the substrate is observed during the experiment.

Taking into account the desorption temperatures from the QCMB, our results compare well with those previously published in literature on this area (Bar-Nun et al. 1985; Yoshinobu & Kawai 1996; Collings et al. 2003).

The results of thermal desorption after co-deposition of $\text{CO}_2:\text{CH}_4$ are presented in Figure 2 (right panel).

From the plot, we can observe two features from the frequency variations that we can associate to CH_4 molecules desorbing from the mixture. To isolate the signal due to CH_4 , we remove the contribution of temperature and CO_2 release subtracting the data showed in Figure 2 (left panel), obtaining Figure 3. In this plot, two previously mentioned features (the peaks at 50 and 75 K) are clearly visible. Both signals appear at temperatures higher than the sublimation point of CH_4 under

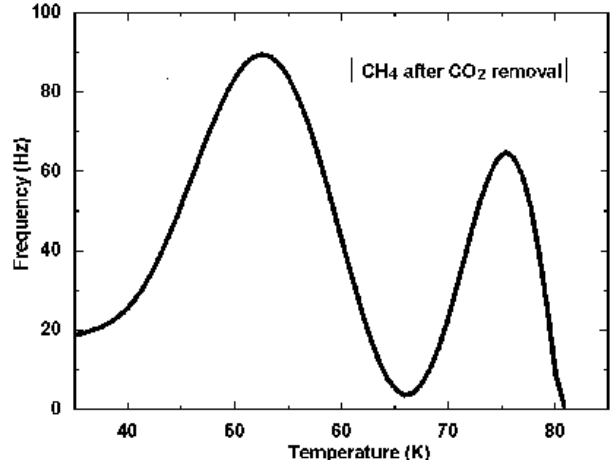


Fig. 3.— CH_4 remnants detected by QCMB frequency variations after CO_2 removal and thermal correction.

our experimental conditions. Therefore, in some way, CO_2 has retained CH_4 molecules.

Since this technique (QCMB) does not allow us to distinguish different molecules desorbing at the same time, we needed an additional technique to know whether CH_4 is retained up to the characteristic sublimation temperatures of CO_2 (91 K in our experimental conditions). Mass spectroscopy allows us to detect that part of CH_4 desorbs at the same temperature that CO_2 sublimates (Figure 4). We are able to conclude this because the behavior of CO_2 and CH_4 partial pressure during thermal desorption from 90 to 110 K are similar. Additionally, it allowed us to confirm that the peaks at 50 and 75 K are due only to CH_4 although they appear at slightly shifted temperatures due to the configuration of our system.

To explain CO_2 matrix ice, in the literature an amorphous CO_2 structure is generally proposed by authors, some of them arguing that no crystals exist in the whole film when the film is grown at temperatures below 30 K (Sandford & Allamandola 1990) but others suggest that this amorphous structure arises from a compilation of small crystallites randomly oriented (Schulze & Abe 1980).

Taking into account our experiments and the previous models just quoted, below we enumerate and describe the three characteristic temperatures that we have found with the QCMB and the QMS:

TEMPERATURE 1: Around 50 K, the first release of the gas trapped by CO_2 takes place. This desorption occurs at higher temperatures than the sublimation point of CH_4 and takes place at the temperature reported previously by other authors as the transition between amorphous and crystalline phase of solid CO_2

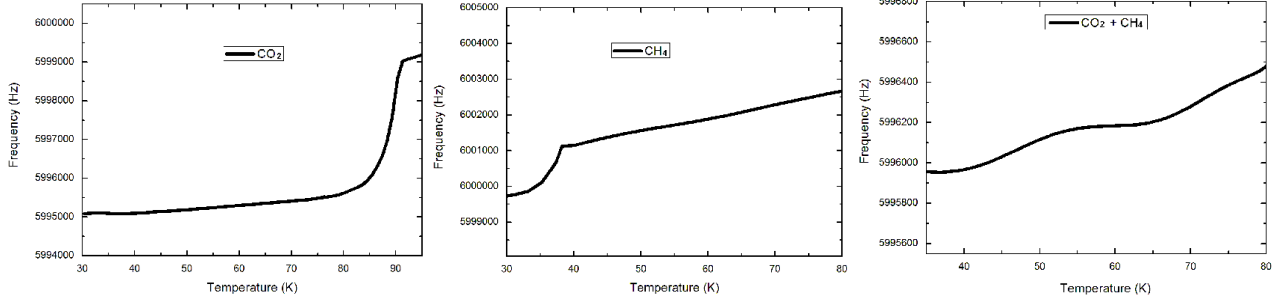


Fig. 2.— Frequency variations of QCMB during thermal desorption process of gases under our laboratory conditions: Left panel: CO₂; center panel: CH₄; right panel: mixture CO₂:CH₄ (95:5).

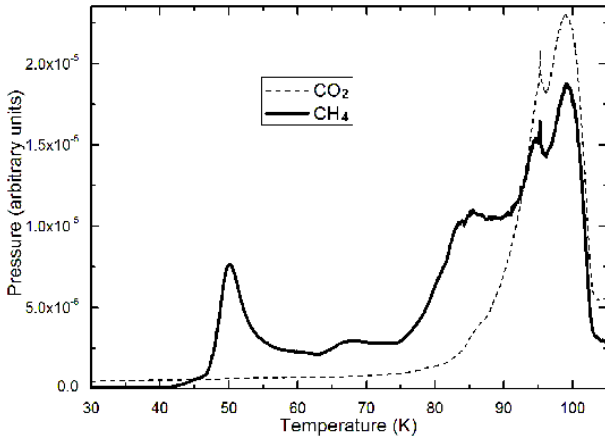


Fig. 4.— Thermal desorption process of CO₂:CH₄ mixture recorded as partial pressure versus temperature.

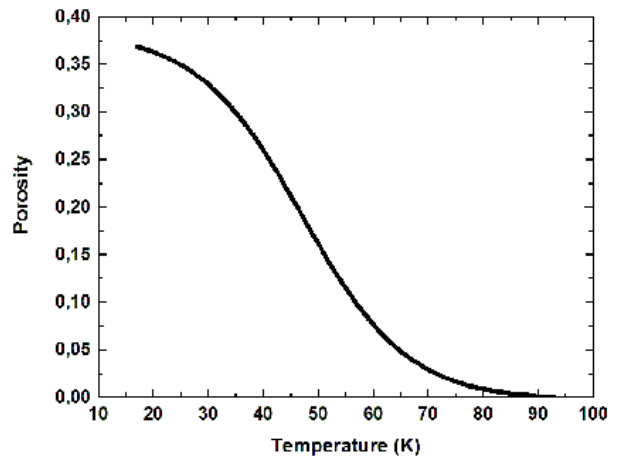


Fig. 5.— CO₂ porosity from Satorre et al. (in preparation). We have taken our maximum experimental density as the maximum density in the porosity equation.

(Falk 1987). This kind of physical process has been named molecular volcano by (Smith et al. 1997) in the case of CCl₄ in water.

In the other model, when the temperature increases the crystallites could undergo a process leading to the structure compacting from a highly porous one to a less porous structure. Molecules of CH₄ would be linked to the surface of CO₂ (we understand as a surface the upper rough surface and open pores). The increasing density involves a variation in the characteristics of the pores, therefore the temperature increase produces the effect that molecules which were previously retained now sublime.

TEMPERATURE 2: A second release occurs at around 75 K. This fact coincides with the compacting of the structure that arises from the continuous variation of the CO₂ density, as can be seen when the porosity reaches the minimum value at around 75 K (Figure 5). We calculate the porosity as defined by the equation: $p = 1 - \frac{\rho_a}{\rho_i}$, (where ρ_a is the density obtained at

certain temperature of deposition and ρ_i is the asymptotic or maximum density), where $\rho_i = 1.5 \text{ g cm}^{-3}$. To perform this plot the maximum density that we have taken in this equation is the maximum experimental density obtained by double angle interferometry and a QCMB when the CO₂ is deposited at twelve different temperatures ranging from 15 to 85 K (Satorre et al. in preparation) where the only purpose is to show how the porosity reaches the minimum value at around 75 K, not to give a quantitative value of the porosity.

The work of Schulze & Abe (1980) supports our findings as they show that the density varies more than 50% between deposits from 10 K to 80 K reaching the maximum density at around 75 K.

TEMPERATURE 3: Finally, CH₄ molecules are detected when the CO₂ desorbs at 90 K. Those interstitial molecules, which are the most strongly trapped and have remained inside the structure after crystallization, are thus retained until desorption of the CO₂ matrix.

4 Conclusions

Our experiments have been used to study the desorption properties of CH_4 in CO_2 matrix and to study the structure of CO_2 itself and its interaction with different types of molecules. These interactions are very complex and requires further complementary studies (thermal desorption with other molecules and in different proportions, electron diffraction,...) considering that the structure of CO_2 accreted at low temperatures is not clear. However some general outlines can be extrapolated from our results. We found different intervals of temperature where CH_4 is released at higher temperatures than its sublimation point implying several kinds of interactions responsible for retaining this molecule within the CO_2 structure.

CO_2 matrices could efficiently retain simple molecules. From the result obtained with CH_4 we expect that there are different mechanisms involved producing various temperatures of desorption.

A first mechanism could be associated to the beginning of CO_2 crystallization with the adsorbed molecules that bring about an offset to higher temperatures (50 K) than their characteristic sublimation temperature.

Another kind of interaction can be seen from the onset of the peak at 70 K corresponding to the most compacted possible structure of CO_2 .

Finally, the molecules more strongly retained in the structure are revealed from the last sublimation at 90 K.

Once the shifts in the sublimation temperature are described many astrophysical applications can be found. It is generally assumed that the volatile components (N_2 , O_2 , CO , CH_4 ...) on ice layers of interstellar dust grains sublime below 40 K. This assumption may be an oversimplification of the behaviour of such ices. An important proportion of them may be desorbed into the gas phase at higher temperatures as a result of adsorption on the porous surface or entrapment within the closed pores of the hydrogenated layer (H_2O) until it desorbs (Collings et al. 2004). The release of material into the gas phase at higher temperatures than previously thought may have a significant impact on the gas-phase chemistry. For example, this has been applied to massive protostars (Viti et al. 2004). But this retarding of the sublimation, as is evident from the results reported in this paper, would not be exclusive to the hydrogenated layer (H_2O), but would also be important in the case of the CO_2 ice. This finding would have to be taken into account in appropriate scenarios.

Furthermore it would be of interest to study the kinetics of chemical processes at temperatures at which it was previously thought to be impossible to retain some volatile elements. As Fraser & van Dishoeck

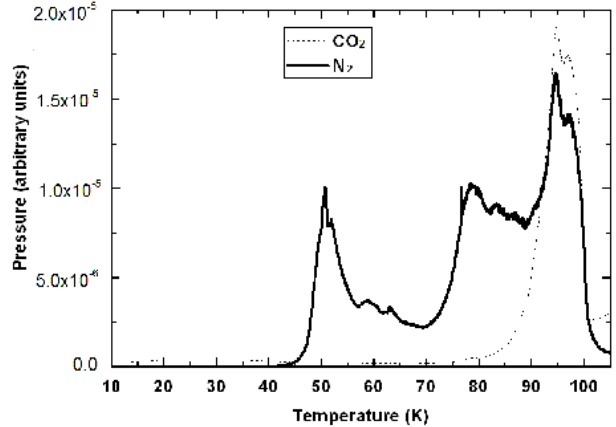


Fig. 6.— Thermal desorption process of $\text{CO}_2:\text{N}_2$ mixture recorded as partial pressure versus temperature.

(2004) show, the chemistry is related with the adsorbed molecules and physical processes (diffusion, adsorption,...) in the ices.

It is also possible to study the geographical composition of ices in some solar system satellites such as Triton, where Quirico et al. (1999) explored the possibility that CO_2 is segregated in a separated terrain from the other terrains, one composed of water and the other of a mixture of N_2 , CH_4 and CO due to difference volatility of molecules. In Triton CO_2 may be produced from CO by means of, for example, chemical reactions with OH radicals as suggested by Cruikshank et al. (1993) or produced by ion irradiation (see for example Palumbo & Strazzulla (1993)). In both cases the possibility that part of the finally segregated CO_2 retains a small percentage of volatiles within its structure should not be discarded. In the light of our results and taking into account that the model of Quirico et al. (1999) fits well but still leaves some discrepancies with the spectra of Triton, new mixtures with low percentages of volatiles could be good laboratory candidates to complete the current models.

Previous applications should be taken as examples, but the experiments presented here are relevant for any astrophysical environment in which the presence of CO_2 ice is important. It should be taken into account that the conclusions drawn in the present paper could be applied not only to CH_4 molecules but could be enlarged to other simple molecules with similar characteristics present in astrophysical environments such as N_2 whose initial preliminary results (See Figure 6) similar to those of CH_4 have corroborated the shift in temperature although further experiments would be necessary to confirm this.

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